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**(54)** **Elastomers.**

**(57)** Elastomers are prepared from high molecular weight relatively rigid difunctional compounds and low molecular weight compounds selected from diacids, diols, diamines, hydroxyacids, hydroxyamines and aminoacids.

**EP 0 267 773 A2**

## Description

ElastomersBACKGROUND OF THE INVENTIONField of the Invention

This invention provides novel elastomeric polymers from certain high molecular weight relatively rigid difunctional compounds and certain low molecular weight difunctional compounds. These elastomers are useful for fibers, films or molded products.

Description of the Prior Art

It is known from the prior art to produce elastomers by polycondensation of diesters of high molecular weight relatively rigid dicarboxylic acids with poly(alkylene oxide) glycol in substantially equimolar proportions. The present invention permits one to avoid the use of presynthesized macrodiol and to limit the amount of the expensive high molecular weight and relatively rigid component required to obtain elastomeric properties.

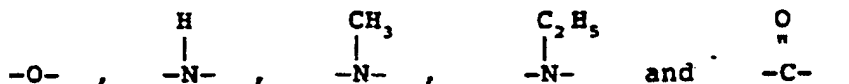
SUMMARY OF THE INVENTION

This invention provides a new elastomer which is characterized by the elastomer consisting essentially of

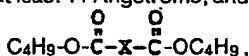
A. from about 5 to 25 weight percent of -X-units where -X- is part of a repeat unit having the structural formula



where -Y- and -Z- are independently selected from



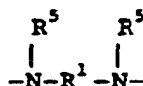
-X- is a divalent organic radical consisting of a chain of ring structures except for trans-amide, carbonyl, trans-vinylene, azo (i.e., -N=N-) and azomethine (i.e., -HC=N-) linkages which may be present and whose shortest length between centers of its terminal junctions measured from a Dreiding model laid flat is at least 11 Angstroms; and when -X- is in the compound:



the compound exhibits a melting point that is at least about 225°C; and

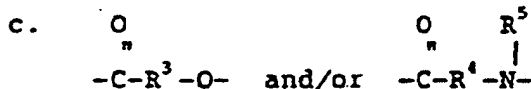
B. at least 75 weight percent of units selected from the following

a.  $-O-R-O-$ , and/or

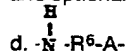


and

b.  $-\overset{\overset{O}{||}}{C}-R^2-\overset{\overset{O}{||}}{C}-$  and/or  $-\overset{\overset{O}{||}}{C}-$ , in which both free bonds are connected to oxygen and/or nitrogen, and/or



and optionally an effective amount of



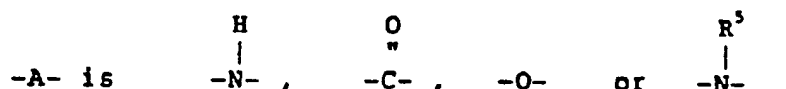
wherein

R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each aliphatic divalent organic radicals, having from 2 to 15 carbon atoms within the chain, with each having a molecular weight of under 450,

R<sup>5</sup> is a hydrocarbon radical,

R<sup>6</sup> a divalent aliphatic or cycloaliphatic radical having 1 to 15 carbon atoms, or a divalent aromatic radical containing 1, 2 or 3 six-membered rings, the rings being non-substituted or substituted with monovalent or divalent alkyl radicals having 1 to 4 carbon atoms, provided that when the alkyl is divalent, one of the

valencies is connected to the -NH- radical or to the -A- radical, and

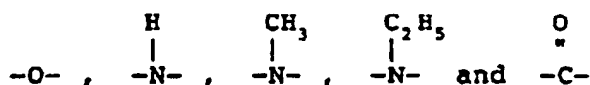


Usually, the d. units amount to 1 to 15% by weight of the polymer. It will be understood, of course, that the polymer must be balanced stoichiometrically. The invention also includes fibers, films, or molded articles from the polymers and processes for manufacture of the polymers.

#### DETAILED DESCRIPTION OF THE INVENTION

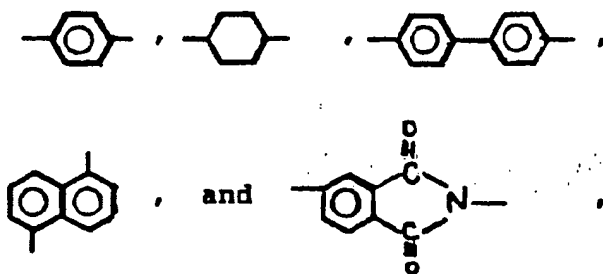
The novel polymer of this invention is an elastomer. By this is meant a polymer which, free of diluents, retracts to less than 1.5 times its original length within one minute after being stretched at room temperature to twice its length and held for one minute before release. This definition corresponds to that given in "ASTM D1566-83a" for a modified rubber. Polymers of the invention are useful in a number of end use applications. Hot melt adhesives, tubing and injection moldings and melt-spun elastic fibers are among such uses. The polymer should preferably have an inherent viscosity of at least 0.55 dL/g when measured as described below.

The polymer is basically comprised of two components, a "hard" segment and a "soft" segment. The "hard" segment corresponds to -X- in units having the formula -Y-X-Z-, the -X- units being present in the polymer in an amount of from about 5 to 25% by weight. The groups -Y- and -Z- are independently selected from



and are attached directly to -X-, or may be separated therefrom by spacer groups (not part of -X-) such as one or more methylene groups. The symbol -X- is a divalent radical whose shortest length between centers of its terminal junctions is at least 11 Angstroms as measured flat, or as flat as can be, with "Dreiding Models" which are constructed to be in precise scale to the actual inter-atomic distances. This technique is known in the prior art and is described in the article by Andre S. Dreiding, *Helv. Chim. Acta* 42, 1339 (1959). The Dreiding models can be conveniently constructed from units obtained from Brinkman Instruments Inc., Cantiague Road, Westbury, NY. The terminal junction is the ring carbon atom of -X- that is attached to the functional group -Y- or -Z- as shown in formula (I) below or any carbon of -X- that is attached to the -Y- or -Z- group, as shown in formula XI below.

Basically, -X- is a radical made up of a chain or backbone of ring structures. The rings of the structure can be fused or not fused. When not fused, the rings are connected to each other within -X- by trans-amide, carbonyl, trans-vinylene, azo or azomethine linkages. The ring structures, which may be, but preferably are not, substituted, include



among others.

The "hard" segment is further characterized by the melting point of the dibutyl ester of the diacid

$\text{HO}-\text{C}(=\text{O})-\text{X}-\text{C}(=\text{O})-\text{OH}$  where -X- is as defined above. The present invention requires this dibutyl ester to have a melting point of at least about 225°C. measured as described below.

Dibutyl esters are prepared in a manner apparent to those skilled in the art. For example, the dibutyl esters of bis-trimellitides are prepared by reaction of two moles of the mono-butyl ester of trimellitic anhydride with one mole of the appropriate diamine. The mono-butyl ester of trimellitic anhydride is formed by reaction of one mole of trimellitic anhydride acid chloride with one mole of n-butanol.

Dibutyl esters of diacids based on the reaction of two moles of p-aminobenzoic acid and one mole of a dianhydride are made by reaction of two moles of the mono-butyl ester of p-aminobenzoic acid and one mole

of the dianhydride.

A number of -Y-X-Z- units are listed below as follows:

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terminal junction

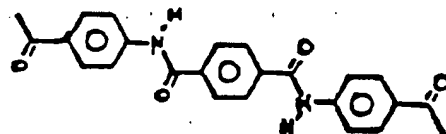
terminal junction

(I)

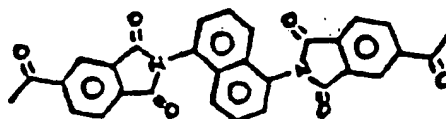
(II)

(III)

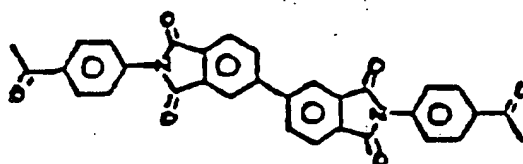
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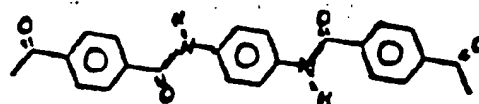
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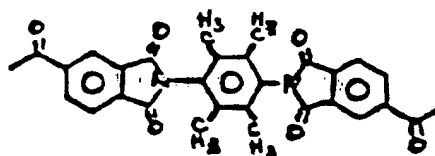
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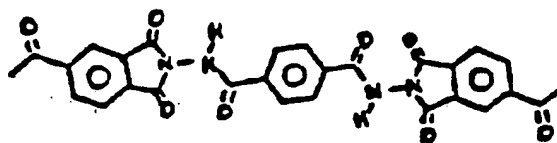
(VII)



(VIII)

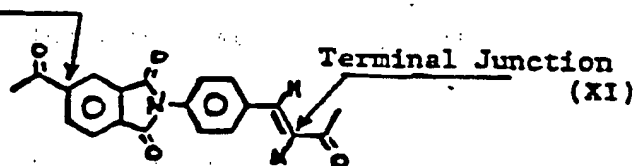


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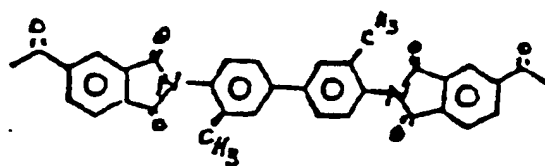


(X)

Terminal Junction

Terminal Junction  
(XI)

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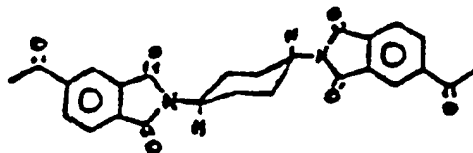


(XII)

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and

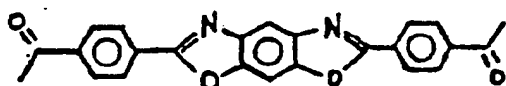
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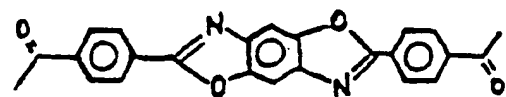
(XIII).

The following list of units also would be expected to meet the requirements for the -Y-X-Z-

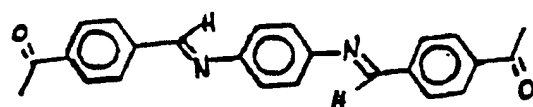
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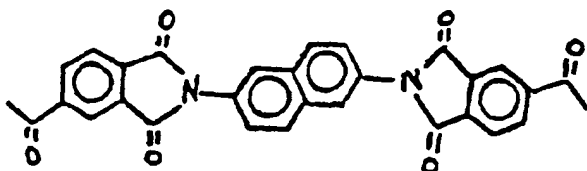
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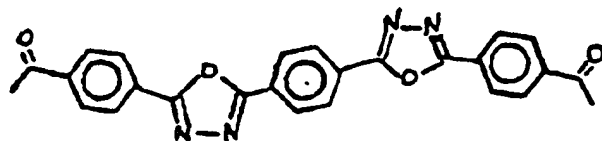
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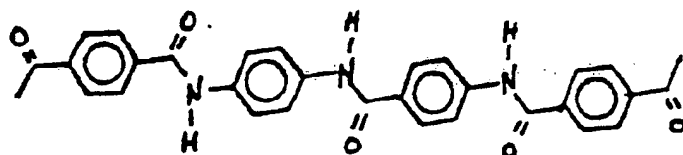
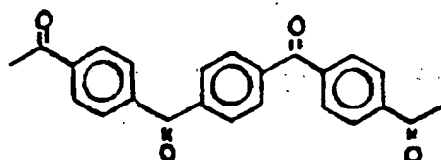
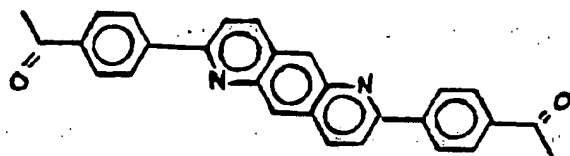
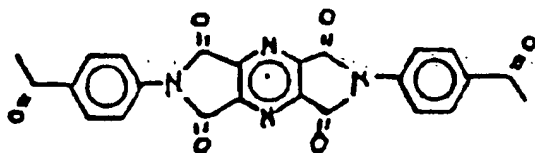
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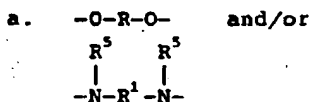
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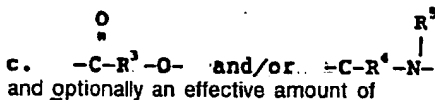
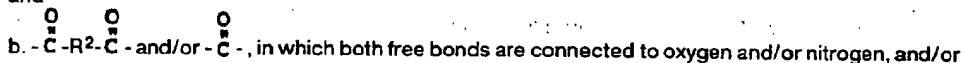
The -Y-X-Z- units are residues of diacids, diols, diamines, hydroxyacids, hydroxyamines and aminoacids. The compounds that provide the -Y-X-Z-units are referred to herein as hard segment precursors, abbreviated as "HSP". Such compounds and their preparation are described in the prior art or can be prepared by techniques well known to those skilled in the art. Preparation of compounds which provide -Y-X-Z-units is illustrated in examples which follow. A preferred synthesis procedure involves making such compounds in a polymer reaction medium of ingredients which ultimately provides the soft segment of the polymer.

In the event an -Y-X-Z- unit in diacid or diol form has an undesirably high melting point which interferes with dissolution in the reaction medium, it may be employed or formed in the form of a more soluble derivative, such as the diester in the case of the diacid. In syntheses where -X- contains a plurality of aromatic amide linkages there is a tendency for the hard segment to cleave. Care must be exercised to avoid scission under the polymerization conditions such as by use of less severe reaction conditions as by use of the aliphatic diacid(s) in the form of their dimethyl esters and by use of hindered aliphatic diol(s) such as neopentyl glycol or 1,2-propanediol.

The remainder of the elastomer composition, about 75 to 95% by weight of the polymer, is the "soft" segment, which is substantially amorphous. It has a glass transition temperature below room temperature, and is made up of units a. plus units b. and/or c. plus optional units d. (when present), as follows:



and

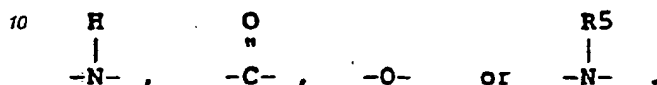


wherein the d. units preferably amount to from 1 to 15 % of the total weight of the polymer and

R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each aliphatic divalent organic radicals, having from 2 to 15 carbon atoms within the chain, with each having a molecular weight of under 450,

R<sup>5</sup> is a hydrocarbon radical,

R<sup>6</sup> is a divalent aliphatic radical having 1 to 15 carbon atoms, or a divalent aromatic radical containing 1, 2 or 3 six-membered rings, the rings being non-substituted or substituted with monovalent or divalent alkyl radicals having 1 to 4 carbon atoms, provided that when the alkyl radical, of unit d. is divalent, one of the valencies is connected to the -NH-radical or to the -A- radical, and -A- is



The term "aliphatic" is intended to include straight chain, branched chain and cycloaliphatic, as well as aliphatic which may be interrupted with -O-, -S-, tertiary nitrogen or may be substituted, as for example, with halogens. Preferably the aliphatic radical is a saturated hydrocarbon, although small amounts of unsaturated units, such as are derived from 2-butene, 4-diol or maleic acid, are also permitted. The R<sup>5</sup> hydrocarbon radical preferably is a phenyl or an alkyl having 1 to 6 carbon atoms. It is expected that if halogen substituents were attached to permitted rings of R<sup>6</sup> of unit d., the resultant polymer would be about equivalent to the same polymer having monovalent alkyl radical substituents on the rings.

The "soft" segment may include minor amounts, i.e., less than about 20% by weight of the soft segment, of units not conforming to these formulas, such as units from hydroquinone, terephthalic acid or higher molecular weight macrodiols, such as polyalkylene ether glycols or macrodiacids, such as "dimer acid", the commercially available diacid obtained by coupling of two long chain unsaturated monocarboxylic fatty acids.

The polymer of the present invention is "stoichiometrically balanced". This means, for example, that the number of moles of unit a. is substantially equal to the sum of the moles of unit b. plus the moles of -Y-X-Z- when both -Y- and -Z- are carbonyl groups, and the number of moles of unit b. is substantially equal to the sum of the moles of unit a. plus moles of -Y-X-Z- where both -Y- and -Z- are



If -Y- is carbonyl and -Z- is

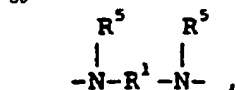


then the number of moles of unit a., if present, will be substantially equal to the number of moles of unit b. similarly, the number of moles of unit d. substantially equals the sum of the moles of unit b. plus the moles of -Y-X-Z- when -A- of unit d. is



If -A- is a carbonyl radical, then the number of moles of unit a., if present, substantially equals the number of moles of unit b.

The unit, -O-R-O-, is the residue of a low molecular weight aliphatic diol. Included among the diols useful in this invention are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-, 1,3-, and 1,4-butylen glycol, 1,6-hexanediol, neopentyl glycol and diethylene glycol. Neopentyl glycol is especially useful. Aliphatic diols having a tertiary nitrogen atom in the chain are also useful. Mixtures of the diols are often used with improved results. Minor amounts of aromatic diols may be included in a diol mixture provided they do not interfere with the desired elastomeric properties. In place of or in addition to the diols, low molecular weight diamines may be employed in the preparation of the polymer. The unit,





represents the residue of suitable low molecular weight aliphatic diamines. Included among such suitable compounds are N,N'-dibutylpentamethylenediamine and N,N'-dimethylhexamethylenediamine. The functional equivalents of the diols and diamines may be used in the preparation. Thus, for example, epoxides can be used in place of the dihydroxy compound, which in the case of phenylglycidyl ether is 1,2-dihydroxy-3-phenoxypropane.

The unit  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{R}^2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$  and the unit  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$  are, respectively, residues of an aliphatic dicarboxylic acid and carbonic acid. Included among the useful acids are succinic, glutaric, adipic, azelaic, carbonic and dodecanedioic acid, as well as their functional equivalents, such as the esters, acid halides and anhydrides thereof. Adipic acid and dibasic acids having at least 7 straight-chain carbon atoms between the carboxyl atoms are particularly useful. Mixtures of acids may be used if desired. Aromatic dicarboxylic acids may be used only in minor amounts in admixture with the low molecular weight aliphatic dicarboxylic acids since larger amounts cause a substantial increase in the glass transition temperature, T<sub>g</sub>, of the elastomer, impairing low temperature, T<sub>g</sub>, of the elastomer, impairing low temperature performance.

The unit,  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{R}^3-\text{O}-$ , is the residue of an aliphatic hydroxyacid. Examples of such hydroxyacids include 12-hydroxystearic acid, 10-hydroxydecanoic acid and 4-hydroxycaproic acid as well as their functional equivalents, such as lactones. Mixtures of hydroxyacids may be used if desired. Hydroxyaromatic acids, such as hydroxybenzoic acid, may be used in minor amounts in admixture with the aliphatic hydroxyacids provided they do not interfere with the desired elastomeric properties. Similarly, the unit,

$-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{R}^4-\overset{\text{R}^5}{\underset{\text{H}}{\text{N}}}-$ , which is the residue of an aliphatic aminoacid may be present in place of or in addition to the  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{R}^3-\text{O}-$  units.

One such aminoacid is N-butyl-6-aminohexanoic acid. R<sup>5</sup> is as defined above.

Optional unit d.,  $-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}-\text{R}^6-\text{A}-$ , is the residue of a low molecular weight primary amine. Suitable compounds for providing the residue include diamines, such as hexamethylene diamine or trans-1,4-diaminocyclohexane, or amino alcohols, such as 3-amino-1-propanol, or amino acids, such as 11-aminoundecanoic acid, 6-aminocaproic acid, p-aminobenzoic acid, 4-methylaminobenzoic acid or 4-aminophenylacetic acid, and functional equivalents, such as ε-caprolactam and the like, or mixtures thereof.

When present, unit d. usually amounts to 1 to 15 percent of the total weight of the elastomer. The amount of unit d. needed to be effective in improving the elastic and set properties of the elastomer depends on, among other things, the particular hard segment, the amount of hard segment and the particular other units present in the elastomer. For example, the improvement is most evident when the amount of hard segment amounts to 15 to 25 percent of the elastomer weight. Preferably, unit d. amounts to 3 to 6 % when the unit d. is the residue of a diamine or of an amino alcohol and 5 to 10 % when unit d. is the residue of an amino acid. Units d. preferably are derived from 3-amino-1-propanol, trans-1,4-diaminocyclohexane, 11-aminoundecanoic acid and 6-aminocaproic acid.

Amorphous soft segments usually are desired for superior elastomer properties. Various techniques can be used to avoid crystallinity in the soft segment. For example, one can use a mixture of aliphatic diols with one aliphatic diacid, or a mixture of aliphatic diacids with one aliphatic diol, or N-alkyl groups in the units a. described above.

The aforementioned units a., b. and c. of the soft segment can be supplied from polyester macromolecules which revert to the diols and diacids (and oligomers thereof) from which they are formed. This reversion can occur in the course of preparation of the thermoplastic elastomer of the present invention. The aforementioned unit d. of the soft segment can be supplied from a short segment (oligomer) of a polyamide which reverts to the amino acid or corresponding diacids and diamines or amine alcohols.

With the diester or diacid hard segment precursors described herein, the elastomers can be made conveniently by conventional esterification and/or ester interchange reactions. One procedure, for example, involves heating at about 200 to 300°C in the presence of a catalyst, (1) the diacid that provides the hard segment, e.g., p-phenylene-bis-(N-trimellitide) which yields (I), with (2) reactants that form the soft segment such as (i) a low molecular weight diol or mixture of diols in molar excess (ii) a low molecular weight aliphatic diacid or mixture of diacids, and (iii) ingredients that yield primary amine units (units d.). Heating is continued until all the water formed by the esterification reaction is distilled off. The heating can require a few minutes or a few hours, depending on the particular reactions taking place. As a result of this procedure a low molecular weight prepolymer is prepared which can then be formed into a high molecular weight copolyester by the procedure described below. If the dimethyl ester of the low molecular weight aliphatic diacid is used in place of the free acid, methanol is evolved instead of water. Also, anhydrides or acid chlorides can be used with or instead of the diacids. Alternatively, the prepolymer can be prepared from the free acids with diacetates to the aliphatic diols (in which case, acetic acid is removed by distillation), or with "ethylene oxide type" cyclic ethers

or with carbonates. If desired, an ester interchange can be performed, for example, by reacting the diacid which provides the hard segment with a high or low molecular weight ester homopolymer or copolymer in the presence of catalyst until randomization occurs. A small amount of low molecular weight aliphatic diacid or diol can be added for stoichiometric balance, if needed.

5 In another alternative process for preparing an elastomer of the invention, the precursors of the high molecular weight diacid and one or more diols providing unit a. are first formed into a slurry after which a catalyst and one or more diacids providing unit b. and one or more primary amine compounds providing unit d. are added. The resultant mixture is then heated to form the prepolymer.

10 The molecular weight of the prepolymer is increased by distilling off the excess diol along with evolved water or methanol. Further esterification and/or ester interchange occurs during the distillation, which causes the molecular weight to increase and the arrangement of the copolyester units to be random. Usually, superior results are obtained when the final distillation or polycondensation is performed at a pressure of less than 5 mm and a temperature in the range of 250 to 300°C for less than 4 hours in the presence of antioxidants such as N,N'-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide). To avoid excessive time periods at high temperatures, with possible accompanying irreversible thermal degradation, it is advantageous to employ 15 a catalyst for the esterification and/or ester interchange reactions. A wide variety of catalysts can be used. Organic titanates, such as tetrabutyl titanate (TBT), used alone or in combination with magnesium or calcium acetates, are preferred when ester interchange is the sole mechanism of polymerization. Inorganic titanates such as lanthanum titanate, calcium acetate/antimony trioxide mixtures and lithium and magnesium alkoxides are representative of other suitable catalysts. When direct esterification (between diols and diacids) is employed in the presence of compounds providing primary amine units d., antimony trioxide is the preferred catalyst.

20 The esterifications or ester-interchanges usually are performed in the melt without added solvent, though inert solvents can be used to facilitate removal of volatile components at lower temperatures. This technique is especially valuable during preparation of prepolymer by direct esterification. However, certain low molecular weight diols (e.g., butanediol) can be conveniently distilled off during polymerization. Batch and/or continuous methods can be used for the various stages of the copolyester polymer preparation. Polycondensation of prepolymer can also be accomplished in the solid phase by heating finely divided solid prepolymer in a vacuum or in a stream of inert gas to remove low molecular weight products.

30 The elastomers of this invention possess many desirable properties. However, it is sometimes advisable to protect certain of the compositions against heat of radiation by ultra-violet light by incorporating stabilizers in the elastomer. Satisfactory stabilizers include phenols and their derivatives, amines and their derivatives, compounds containing both hydroxyl and amine groups, hydroxyazines, oximes polymeric phenolic esters and salts of multivalent metals in which the metal is in its lower valence state. Among such phenol derivatives are 35 4,4'-bis(2,6-ditertiary butylphenol) and 1,3,5-trimethyl-2,4,6-tris-(3,5-ditertiarybutyl-4-hydroxybenzyl)benzene ("AO-330", sold by Ethyl Corp., Baton Rouge, Louisiana). Also suitable are various inorganic metal salts or hydroxides and organic complexes, such as nickel dibutylidithio-carbamate, manganous salicylate and copper 3-phenyl-salicylate. Suitable amine stabilizers include N,N'-bis( $\beta$ -naphthyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine and either phenyl-betanaphthylamine or its reaction products with aldehydes. Mixtures of hindered phenols with esters of thiodipropionic acid, mercaptides and phosphite esters are particularly useful. Additional stabilization to ultraviolet light can be obtained by incorporating various UV absorbers, such as substituted piperidyl derivatives, substituted benzophenones or substituted benzotriazoles.

45 Sometimes, branching agents are incorporated, at a concentration of 0.001 to 0.005 equivalents per 100 g of polymer, to increase melt strength, as disclosed in for example, U.S. Patents 4,013,624 and 4,205,158. Suitable branching agents include polyols having 3 to 6 hydroxyl groups, polycarboxylic acids having 3 or 4 carboxyl groups or hydroxy acids having a total of 3 to 6 hydroxyl and carboxyl groups. Among such polyols are glycerol, trimethylol propane, 1,2,6-hexanetriol, 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane, sorbitol, and pentaerythritol. Suitable polycarboxylic acid branching agents include hemimellitic acid, trimellitic acid, 50 trimesic acid, 1,1,2,2-ethanetetra-carboxylic acid, pyromellitic acid, 1,1,2-ethanetricarboxylic acid, 1,2,3,4-cyclopentanetetra-carboxylic acid, and 1,3,5-pentanetricarboxylic acid. Although the acids can be used as such, preferably they are used in the form of their lower alkyl esters.

Properties of the elastomers of the invention can be modified by incorporation of various conventional inorganic fillers, such as carbon black, silica gel, alumina, clays and reinforcing fiber (e.g., glass). Usually, 55 these additives increase the elastomer modulus at various elongations. The desired hardness of the elastomer can be obtained by blending elastomers of the invention having different percentages of hard and soft segments.

A method for improving the tenacity and set of fibers or films made from these polymers comprises heating the fibers or films for at least two hours at temperatures of at least 150°C in an inert atmosphere (as disclosed 60 in U.S. Patent 3,801,547). If desired, slight or moderate tension can be applied during heating. Excessively long heating periods and excessively high temperatures should be avoided to prevent deterioration of the polymer or of the fiber or film made from the polymer.

65 The elastomers of the invention which contain effective amounts of primary amine units d. in its soft segments, compared to elastomers of like composition that do not contain such units d., can form tapes and filaments with significantly improved properties. For example, elastomers containing such primary amine units

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